

SCIENCE FOR GLASS PRODUCTION

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PARTICULARS OF FOAM GLASS MANUFACTURE FROM ZEOLITE-ALKALI BATCH

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The particulars of thermally activated foaming of zeolite-alkali batch are examined. It is found that carbonation of free NaOH with formation of hydrated sodium-carbonate — $\text{Na}_3[\text{CO}_3][\text{HCO}_3] \cdot 2\text{H}_2\text{O}$ — occurs in dry granular batch kept in air. The same process also occurs with NaOH occluded by in-crystalline pores and zeolite channels. Sodium carbonate contained in in-crystalline pores and zeolite channels comprises an additional source of foaming agent — CO_2 . This makes it possible to obtain foam glass with density 100–150 kg/m³ from zeolite-containing rocks.

Key words: foam glass, zeolite-containing rocks, carbonation of NaOH, melting, pore-forming gas.

Foam glass block and granular foam glass are biologically safe and the most durable heat-insulating construction materials. Even though it has definite advantages over other heating-insulating materials the few producers in Russia manufacture only granular foam glass using the simplest technology based on domestic equipment. The high cost of energy in glassmaking and limited stocks of cullet impede expansion of foam glass production.

Methods of manufacturing foam glass from naturally occurring raw materials without preliminary melting are being developed in order to fill the shortage of heat-insulation materials. Siliceous (opoka, tripoli and diatomite) and aluminum-silicate rocks serve as raw materials. Of the great diversity of aluminum-silicate raw materials tuffaceous zeolite-containing rocks (ZR) are the most promising. In contrast to siliceous rocks many types of natural zeolites are capable of foaming at the natural melting temperature — 1100–1200°C. The nature and mechanism of thermally activated foaming of natural zeolites have been studied and are presented in [1–4]. Technologies for fabricating different types of porous construction materials — block and granular — under the trademark Sibeerfoam® from zeolite-containing nature raw materials at the natural melting temperature of ZR have been developed [5–7]. Even though the foam materials obtained by means of the high-temperature technology de-

veloped are of high quality, the manufacturing plant was not put into operation because of the high cost of energy for firing and a lack of standard furnace equipment.

In order to manufacture foam materials from natural raw material at the same temperature at which foam glass is obtained by the conventional powder technology from glass (750–800°C), materials that lower the melting temperature of the rock are added to the silica-containing compositions. To prepare foam materials from siliceous raw materials sodium hydroxide is, as a rule, used as a flux that not only lowers the melting temperature of the rock but also forms a source of foaming gas — hydrated sodium polysilicates [8].

It is shown in [9] that the chemical interaction of sodium hydroxide with the mineral components of ZR in moist batch differs from the interaction with siliceous rock — opoka. It was also established that hydrated sodium carbonate forms in air-cured dry zeolite-alkali batch. The particularities of ZR must be taken into account in order to develop a technology for fabricating foam glass from it.

In the present article we present the results of an investigation of the effect of carbonation of alkali in zeolite-containing batch on its foaming intensity and the particularities of the foam glass obtained from zeolite-alkali batch.

METHODS OF STUDY AND RAW MATERIALS CHARACTERISTICS

The initial properties of the ZR and the processes occurring in it in an alkaline medium were analyzed by the x-ray

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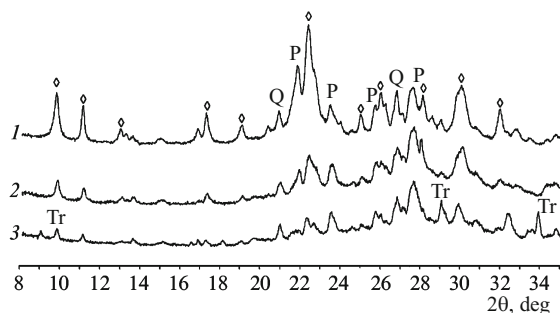


Fig. 1. Diffraction profile: 1) ZR from the Kholinskoe deposit; 2) dry batch with the composition ZR + NaOH; 3) dry batch with the composition ZR + NaOH after standing in air; ◇) clinoptilolite; Q) quartz; P) plagioclase; Tr) trona ($\text{Na}_3[\text{CO}_3][\text{HCO}_3] \cdot 2\text{H}_2\text{O}$).

fluorescence method (VRA-20R x-ray analyzer), powder x-ray diffractometry (Thermo Scientific ARL-X'tra diffractometer), IR spectrometry (FT-IR VERTEX Fourier spectrometer) and scanning electron microscopy (Philips XL30-FEG).

Zeolite-containing rock from the Kholinskoe deposit was used as the main aluminum silicate raw material. The chemical composition of the zeolite-containing rock is presented in Table 1.

The rock contains crystalline phases — zeolite (clinoptilolite), plagioclase and quartz (Fig. 1). The content of clinoptilolite in tuff is 50 – 55%.² The peak in the mass losses at 500°C in the DTG curve shows that a very small amount of clayey minerals is also present in the rock (Fig. 2a). The DTG curve at low temperatures is typical for clinoptilolite zeolites [10]. The losses near 100°C are related with the removal of physically adsorbed water. In this temperature range some of the zeolitic water is removed. The shoulder at 300°C also corresponds to the loss of zeolitic water.

The ZR was comminuted in a vibratory mill to specific surface area 32 m²/g. The powder was moistened with a water solution of NaOH to a plastic state with 82% rock and 18% NaOH in the dry state. Granules with diameters 4 – 5 mm were formed immediately from the wetted paste and dried at 100°C to the air-dry state. The freshly dried granules as well as granules after standing in air (to formation of hydrated sodium carbonate in them) were fired at temperatures in the range 300 – 850°C in 100°C steps to 700°C and 50°C steps at higher temperatures, with 10-min soaking at each temperature. The intensity of the foaming

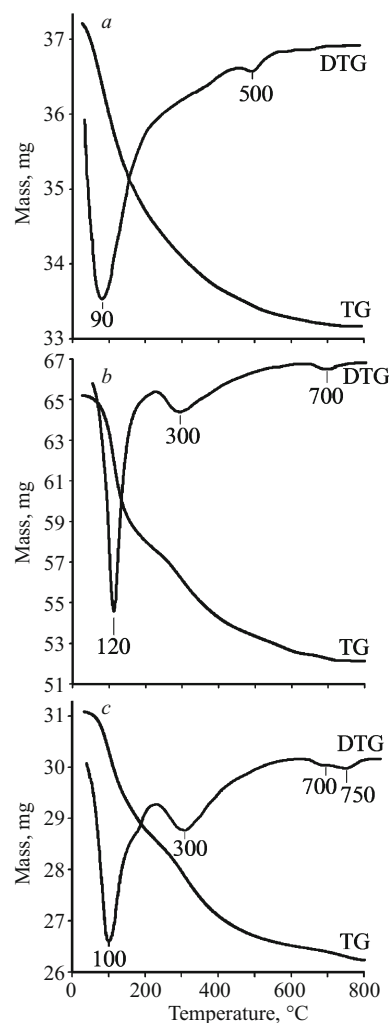


Fig. 2. DTG and TG curves: a) ZR from the Kholinskoe deposit; b) dry batch with the composition ZR + NaOH; c) dry batch with the composition ZR + NaOH after standing in air.

was determined according to the density of the granules after firing.

To clarify the role of hydrated sodium carbonate in the foaming process granules were also prepared from a composition with soda ash: 78% ZR and 22% Na_2CO_3 . At this concentration the molar content of Na_2O in the alkali and carbonate compositions was the same. The mixture was moistened to the molding moisture content by a water solution of liquid glass with 1 : 1 thinning with water. Granules were formed from the paste, heated at 50°C in a closed state to transformation of Na_2CO_3 into hydrated sodium carbonate

² Here and below the content by weight, wt.%.

TABLE 1. Chemical Composition of Zeolite-Containing Rock

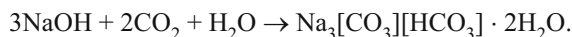
Oxide content, wt.%, dry matter										
SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	other
69.24	12.72	0.13	1.17	0.06	0.26	2.51	1.53	4.58	0.02	7.74

(trona), dried and fired simultaneously with the alkali compositions.

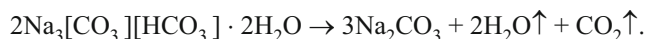
RESULTS AND DISCUSSION

A particularity of foam-glass manufacture from zeolite-alkali compositions is carbonation of alkali in dry batch when held in air [9]. X-ray diffractometry shows hydrated sodium carbonate in such batch — trona ($\text{Na}_3[\text{CO}_3][\text{HCO}_3] \cdot 2\text{H}_2\text{O}$). For alkali compositions only partial amorphization of clinoptilolite is observed in freshly dried granulated batch; there is no trona in it (see Fig. 1).

It is known that alkali sorbs carbon dioxide. In [9] it is established that when ZR powder is wetted with a water solution of sodium hydroxide the NaOH transforms only partially into a bound state — water sodium polysilicates ($\text{Na}_2\text{O} \cdot m\text{SiO}_2 \cdot n\text{H}_2\text{O}$). A large part of the NaOH is found in a free state in batch with a film distribution over the powder particles. The presence of free alkali in dry granules makes it possible to represent the formation of trona in them by the usual interaction of sodium hydroxide with carbon dioxide gas and water vapor from air:



The thermally activated decomposition of trona proceeds by well-known decomposition reactions of hydrocarbonate in the temperature range 100 – 200°C:



Heated to 1000°C sodium carbonate decomposes into carbon dioxide gas and sodium oxide: $\text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} + \text{CO}_2\uparrow$.

Pure soda ash does not decompose in the temperature range 750 – 800°C. However, low-melting sodium aluminum-silicates start to form in this temperature range when the mixture ZR + Na_2CO_3 is heated. This process probably initiates the decomposition of sodium carbonate before melting of the paste and formation of closed pores. As a result CO_2 is released into the atmosphere and does not participate in pore formation. The only source of pore-forming gases in such a batch is the hydrated aluminum-silicate surface of the post-zeolite component. For this reason, at the same Na_2O molar content pore-formation in the composition ZR + Na_2CO_3 is always much weaker and proceeds at higher temperature than in ZR + NaOH. At the same time the foaming intensity of air-carbonated zeolite-alkali batch is higher than that of fresh batch in which carbonation of the alkali has not occurred (Fig. 3). This shows that some sodium carbonate remains in the carbonated zeolite-alkali composition to the melting temperature of the batch with CO_2 being released in expanding closed pores. Thermogravimetric and IR-spectroscopic studies confirm this.

The local minimum at 500°C in the DTG curve of ZR + NaOH granules without soaking in air vanishes, which indicates breakdown of the clayey minerals in an alkali medium,

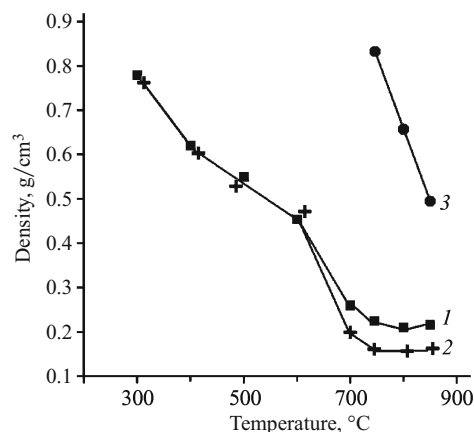


Fig. 3. Temperature variation of the density of the granules: 1) granules freshly prepared from the composition ZR + NaOH; 2) ZR + NaOH granules after standing in air with trona formation; 3) ZR + Na_2CO_3 granules.

and two new minima associated with mass losses appear: a wide well-resolved minimum at 300°C and a weak minimum at 700°C (Fig. 2b). The mass losses at 300°C are due to dehydration of hydrated sodium polysilicates formed in a moist alkali composition. It is due to precisely sodium polysilicates (liquid glass) that pore formation of alkali batch starts already at 300°C, long before melt appears. The minimum at 700°C is associated with de-hydroxylation of the silicate surface of the post-zeolite component ($\equiv\text{Si}-\text{OH} + \text{HO}-\text{Si}\equiv = \text{SiO}_2 + \text{H}_2\text{O}\uparrow$). This temperature corresponds to the initial stage of melting of the composition. The release of a gas phase, coinciding in time with the appearance of melt, is accompanied with enlargement of the pores in the composition and a decrease of the density of the foam glass formed.

On the DTG curve of the carbonated zeolite batch (Fig. 2c), in addition to the mass-loss maximum at 700°C there appears a new maximum at 750°C, which likewise is associated with an increase of the foaming intensity (Fig. 3). Another additional pore-forming gas in such a batch could be CO_2 , released during the decomposition of the sodium carbonate remaining up to the indicated temperature.

IR-Spectroscopic analysis confirms this supposition. In the IR-spectrum of carbonated unfired zeolite-alkali granules, aside from absorption bands typical for clinoptilolite zeolite (470, 610, 727, 794, 1050, 1212 and 1636 cm^{-1}), there appear additional bands of stretching vibrations — an intense band $\nu_3 \text{CO}_3$ near 1454 cm^{-1} and a weak band $\nu_2 \text{CO}_3$ near 880 cm^{-1} . After such a composition is fired at 750 cm^{-1} a weak absorption band $\nu_3 \text{CO}_3$ near 1454 cm^{-1} still appears in the spectrum (Fig. 4).

In the electronic photographs of the cleavage face of carbonated zeolite-containing granules trona appears in the form of micron-size needle formations emanating from the pores of the aluminum-silicate matrix (Fig. 5a). In the composition ZR + Na_2CO_3 , where hydration of the soda ash oc-

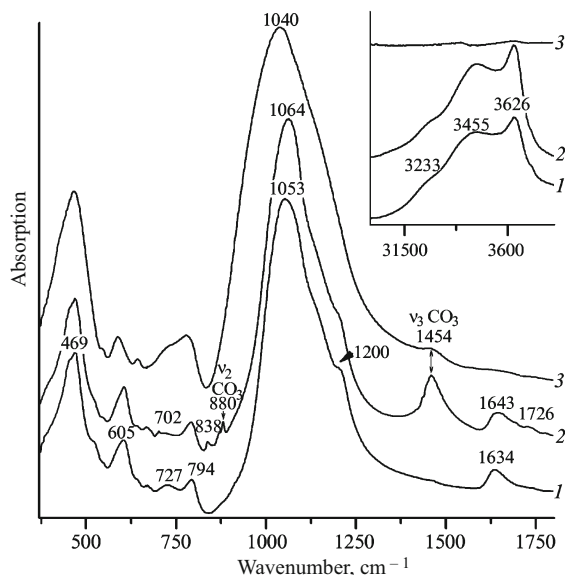


Fig. 4. IR-Spectra: 1) ZR from the Kholinskoe deposit; 2) carbonated composition ZR + NaOH; 3) carbonated composition ZR + NaOH after firing at 750°C.

curred in a moist medium, trona forms in the form of plate-shaped formations filling larger pores between ZR particles (Fig. 5b).

The morphological differences between trona in the two states do not explain the fact that part of the sodium carbonate remains to 750°C only in granules with zeolite-alkali composition. In such a composition Na_2CO_3 can be found

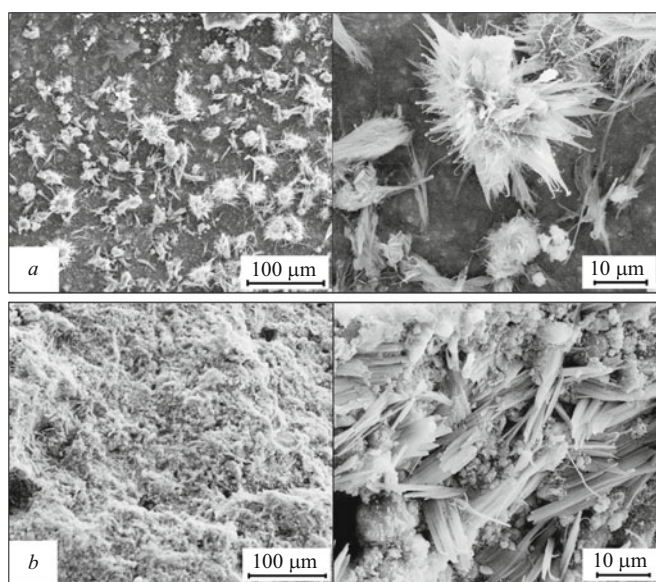


Fig. 5. SEM images of the cleavage faces of granules with the compositions: a) ZR + NaOH after soaking in air with trona formation and b) trona formed during heating of the moist composition ZR + Na_2CO_3 .

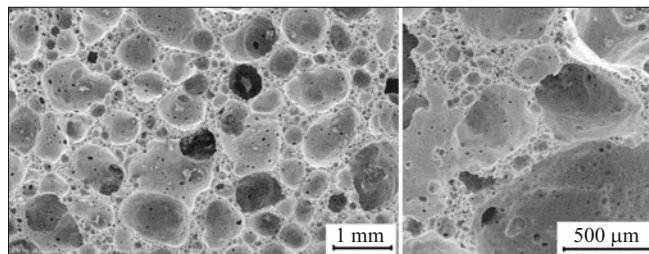


Fig. 6. SEM image of macro- and micro-porous systems of foam glass made from a carbonated zeolite-alkali composition.

only under special conditions. It is well known that in-crystalline voids of zeolites can occlude a nonstoichiometric amount of compounds with uni- and bivalent cations. The dissolved NaOH together with water can fill the intra-crystalline pore space of clinoptilolite. After the granules are dried the occluded sodium hydroxide in pores and channels in clinoptilolite, just as in powder, will unavoidably undergo carbonation due to carbon dioxide in air. This can be promoted by a well-known capability of zeolites to sorb some gases, including CO_2 , from air. On heating, after dehydration and amorphization of clinoptilolite, the pores and channels in the post-zeolite component remain with cationic and carbonate filling. The encapsulation of the carbonate compound in nanopores and channels of the amorphized post-zeolite matter prevents its decomposition to 750°C.

It is well known that the decomposition of carbonate compounds can occur only if the CO_2 released is removed, i.e., the partial pressure of the gas at the location of decomposition decreases. The pyroplastic state of the zeolite-alkali composition at 700 – 750°C makes it possible to decrease the gas partial pressure at the locations of encapsulation of sodium carbonates owing to the expansion of micropores in the inter-pore barriers by the released gas.

The macro- and microporosity of foam glass fabricated from a carbonated zeolite-alkali matrix is shown in Fig. 6. It is characterized by a developed porous system with micron pores in the walls of the micropores and by low density (100 – 150 kg/m³). At the same time through micro-openings, probably formed as a result of the high pressure of carbon dioxide gas in the micropores, can be seen in the pore walls. However, the water absorption of such foam glass corresponds to typical values 2 – 3 vol.%. This indicates that on the whole the foam glass fabricated from carbonated zeolite-alkali batch has a closed system of pores.

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REFERENCES

1. L. K. Kazantseva, I. A. Belitskii, S. N. Dement'ev, et al., "Thermally activated foaming of hydrothermal Ca-Na-zeolites," *Geologiya Geofiz.*, **41**(1), 135 – 141 (2000).

2. L. K. Kazantseva and E. A. Paukshtis, "Thermally induced foaming of clinoptilolite and heulandate zeolitic tuffs," in: *Natural Zeolite for the Third Millennium*, Napoli, Italy (2000), pp. 337 – 349.
3. G. I. Ovcharenko, V. L. Sviridov, and L. K. Kazantseva, *Zeolites in Building Materials* [in Russian], Izd. Altaisk. GTU, Barnaul (2000).
4. L. K. Kazantseva, E. A. Paukshtis, and G. P. Valueva, "Foaming ability of zeolitic rocks a function of their composition," *J. Ceram. Proc. Res.*, **5**(4), 321 – 326 (2004).
5. L. K. Kazantseva, I. A. Belitskii, V. A. Kutolin, et al., *Mix for Obtaining Foam Glass, RF Patent No. 1708784, MPK C03C11/00* [in Russian], published January 30, 1992.
6. L. K. Kazantseva, I. A. Belitskii, Z. I. Koridze, et al., *Raw Materials Mix for Fabricating Porous Fill, RF Patent No. 2023702, MPK C04B14/14* [in Russian], published November 30, 1994.
7. I. A. Belitskii, A. V. Gorbunov, L. K. Kazantseva, and B. A. Fursenko, *Mix for Foam Glass Production, RF Patent No. 2033982, MPK C03C11/00* [in Russian], published April 30, 1995.
8. A. A. Ketov, "Obtaining building materials from hydrated polysilicates," *Stroit. Mater.*, No. 11, 22 – 24 (2012).
9. L. K. Kazantseva, D. V. Zheleznov, Yu. V. Seretkin, and S. V. Rashchenko, "Formation of a source of foaming gas by wetting natural aluminum-silicates with NaOH solution," *Steklo Keram.*, No. 10, 37 – 42 (2012); L. K. Kazantseva, D. V. Zheleznov, Yu. V. Seretkin, and S. V. Rashchenko, "Formation of a pore-forming gas source by wetting natural aluminum-silicate with NaOH solution," *Glass Ceram.*, **69**(9 – 10), 353 – 359 (2012).
10. D. W. Breck, *Zeolite Molecular Sieves* [Russian translation], Mir, Moscow (1976).